

# Study on temperature-enabling dynamics liquid chromatography and its application in uranium isotopes separation\*

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Separation of uranium isotopes is not only a difficult scientific project, but also an engineering problem. A temperature-enabling dynamics liquid chromatography was designed for uranium isotopes separation based on dynamics liquid chromatography and liquid membrane diffusion model. This work prepared ‘organic’ and ‘inorganic’ chromatography columns filled ABS pellets and SiO<sub>2</sub> pellets, respectively. In order to improve the efficiency of separation, the injection-outflow self-control system and temperature-enabling cells were equipped to chromatography columns. The organic column optimal working conditions obtained by experiments were pH=2, enabling temperature=70°C and injection flow rate=15mL/min. Meanwhile, multi-stage separation experiment verified feasibility of uranium isotopes using organic column, the separation factor can reach 1.0184 and needed over 79 stages to enrich <sup>235</sup>U abundance to 3%. The optimal conditions for inorganic column, determined through prior experiments, were pH=2, enabling temperature=50°C and injection flow rate=15mL/min. Multi-stage separation experiments using inorganic columns achieved a separation factor of 1.0110, requiring over 112 stages to enrich <sup>235</sup>U abundance to 3%. Moreover, a series of mechanism experiments illustrated the mechanism of chromatography and confirmed liquid membrane and silica hydroxyl groups involvement in separation process. These studies identified the temperature-enabling dynamics liquid chromatography can effectively separate <sup>235</sup>U from <sup>238</sup>U, which provided a new research idea in the field of chromatography and isotope separation.

Keywords: Uranium isotopes separation; Dynamics chromatography; Temperature enabling; Maximum front enrichment value; Separation factor

## I. INTRODUCTION

Nuclear energy is one of the most important means of solving the energy shortage in the world today. Nuclear power plants use enriched uranium as fuel and utilize the enormous energy released by the nuclear fission reaction to generate electricity, which is a good solution to the problem of electricity consumption in many regions. However, the abundance of <sup>235</sup>U in nuclear fuel must be enriched to more than 3% before it can be used by nuclear power plants. Therefore, the separation and enrichment of uranium isotopes are essential in the production of nuclear fuel. Uranium, the heaviest element in nature, has a mass difference of only 1% between <sup>235</sup>U and <sup>238</sup>U, which makes the separation of uranium isotopes difficult. Historically, researchers have developed several methods for separating uranium isotopes, including gas diffusion, gas centrifugation, nozzle methods, laser enrichment, chemical separation, electromagnetic separation of isotopes, plasma separation[1–3], etc. The gaseous diffusion method was the first historically developed and applied method, but it has been phased out due to its lower separation

factor, larger plant size, and higher power consumption and cost. Its separation factor is 1.0043 [4, 5]. Gas centrifugation has the smallest energy consumption ratio in the world and is the only method that can still be industrially produced, its separation factor can reach 1.01. But this method requires greater than 2000 separation stages, inconvenient and polluting operations [6, 7]. The chemical methods include chromatographic and extraction were created by Japan and France, respectively. The chromatographic method named Asahi Chemical Enrichment Process (ACEP), which used isotope exchange chromatography for uranium enrichment. ACEP employed a chromatography filled with a unique anion exchange resin. When uranyl ions passed through the column, they were adsorbed at the front end of the resin layer, where isotope exchange reactions occur. Finally, a reducing agent was used to elute the ions. The ACEP method achieved a separation factor of 1.003. Since depleted solution can be recirculated back into the column, the process did not require large-scale cascade device[8, 9]. The extraction method, called Chemical Exchange (CHEMEX), relied on isotope exchange reactions, separating uranium by exploiting differences in isotopic behavior between two immiscible liquid phases. CHEMEX achieves a separation factor of approximately 1.0015, which was relatively low, requiring thousands of stages to reach industrial-level enrichment. Both processes have gradually been replaced by more efficient methods, such as gas centrifugation, due to high energy consumption and complex equipment[10, 11]. Laser method exploits differences in spectral property between <sup>235</sup>U and <sup>238</sup>U. Using uranium as ingredient, a laser with specific frequency ionizes <sup>235</sup>U into <sup>235</sup>U<sup>6+</sup>, which were then collected to achieve separation. The method has an extremely high

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separation factor and requires very few separation stages. However, it is costly, involves complex technology, and demands harsh working conditions[12]. Uranium isotope separation technology has been stagnant for many years, so a new uranium enrichment scheme which is safe, efficient, environmentally friendly, can be produced industrially and has low separation power is still needed[13, 14].

Since the beginning of the 20th century, chromatography has developed continuously and become an important means of separation and analysis, which has been used in many fields such as organic, analytical, chemical, medical, biochemical and environmental protection. Simultaneously, dynamics liquid chromatography is a major branch of chromatography and has been used as a highly efficient means of separating natural macromolecules[15, 16]. Dynamics liquid chromatography is divided into two major categories, hydrodynamic chromatography(HDC) and slalom chromatography(SC), both of which rely on the phenomenon of fluid dynamics within the chromatography to separate the solutes and generally do not involve chemical reactions[17–20].

In this paper, two types of dynamics liquid chromatography columns were fabricated for U isotopes separation, which were filled with ABS(Acrylonitrile-butadiene-styrene copolymer, A: acrylonitrile, B: butadiene, S: styrene ethenylbenzene) plastic and SiO<sub>2</sub>, respectively. Subsequently, a system of separation devices was constructed to cooperate with the column for automatic separation and collection. In the experiments, temperature-enabling method was used to improve the separation efficiency of uranium isotopes, and the separation factor of uranium isotopes was obtained by multistage separation experiment. The most important innovation of this manuscript is the pulse chromatography method, which is to use the principle of chromatography to make the light and low valence substances in the solution at the front end of the column, and the heavy and high valence substances at the back end of the column, and then the light and heavy substances are separated by diverting. Through pulse injection, this separation can be carried out one by one, and each pulse is a separation process. Meanwhile, the effects of liquid membrane and functional groups on the experimental results were discussed to reveal the separation mechanism of the chromatographic column.

## II. THEORY

### 2.1 Liquid membrane tidal diffusion model

Horvath and Lin (1978) proposed that a stagnant layer of nearly stationary mobile phase formed on filling surfaces in liquid chromatography, facilitating substance to transfer and exchange[21]. Previous studies indicated adsorption volumes often exhibited sharp turns and minor fluctuations over time (Supplementary file Fig. 1). During Eu adsorption on D231 resin, a triply charged functional group or cation ionized from the resin, exchanging with Eu in solution. Hydrogen ion concentration influenced this ionization: at pH=4, high hydrogen ion concentration inhibited cation ionization, reducing Eu adsorption and enhancing desorption. Supporting information

Fig. 1 shown the adsorption of Eu by D231 resin as a function of time. Where vertical coordinate was the ratio of Eu concentration at moment t to its initial concentration[22].

Yu et al.[23] proposed a hypothesis for adsorbent adsorption/desorption. They suggested that, in addition to binding/separation within internal pores, the liquid membrane on the adsorbent surface also affected substance diffusion, this process was named “liquid membrane tidal diffusion model (LMTD)”. LMTD included two steps as shown in Fig 1. First step, particles mainly diffused into the liquid membrane located at the fillings; the particles in liquid membrane would then be released into the solution. Second step, particles attached to liquid membrane would further diffuse into the solid internal hole. Simultaneously, the particles would then release from the solid internal hole into the liquid membrane. Afterwards, the liquid membrane tidal diffusion model was further investigated by Haoqi Yu et al.[22] and combined with the non-homogeneous isothermal adsorption to create new kinetic equations, which successfully described concentration fluctuation in the adsorption/desorption process.

Based on previous researches, this work proposed the following hypotheses: As the mobile phase moved in chromatography, a liquid membrane formed on filling surfaces. Uranyl ions entered and were retained in the liquid membrane. Flowing solution carried away some retained uranyl ions while continuously delivering new ones into the liquid membrane. Meanwhile, <sup>235</sup>UO<sub>2</sub><sup>2+</sup> is lighter than <sup>238</sup>UO<sub>2</sub><sup>2+</sup>, which cause <sup>235</sup>UO<sub>2</sub><sup>2+</sup> in the liquid membrane would more easily be moved into mobile phase. It gradually separated <sup>235</sup>UO<sub>2</sub><sup>2+</sup> from <sup>238</sup>UO<sub>2</sub><sup>2+</sup> in chromatography.

### 2.2 Determination of optimal separation conditions

Each pulse is to enter a sample solution, then switch a section of air, and then enter the sample solution of the next section of pulse. The optimum conditions for uranium isotopes separation by two chromatographic columns were obtained through conditional experiments.

The flow rate of the mobile phase, pH value and enabling temperature of dynamics chromatography affect the separation effect of chromatography to a certain extent. In order to obtain the optimal separation conditions for the chromatography, the researchers prepared 10 test tubes to collect the chromatographic effluent in equal volumes. The concentration of <sup>235</sup>U and <sup>238</sup>U in the effluent from each tube (each tube was a separate section) was determined by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS, iCAP PROX Germany), and the separation effect of dynamic chromatography was analyzed. For the purpose of better describing the separation effect of columns on U isotopes, front maximum enrichment value ( $\beta$ ) was used in this paper to judge the chromatographic separation ability with different fillings materials under different operating environments [24], Eq (1)

$$\beta = \frac{\frac{{}^{235}\text{U}}{{}^{238}\text{U}}_s}{{}^{235}\text{U}}{{}^{238}\text{U}}_o} \quad (1)$$

where,  $\frac{{}^{235}\text{U}}{{}^{238}\text{U}}_s$  means the isotopic abundance ratio in



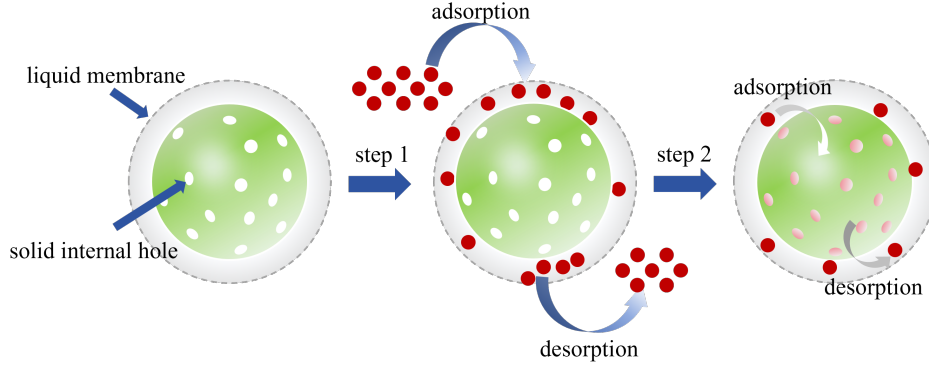


Fig. 1. Schematic diagram of the liquid membrane diffusion tidal model

chromatographic effluents and  $^{235}\text{U}/^{238}\text{U}$  means that in original  $\text{UO}_2(\text{NO}_3)_2$  solution.  $\beta$  values larger than 1.000 means that the  $^{238}\text{U}$  is preferentially enriched in the liquid phase in the front band region and  $^{235}\text{U}$  is enriched in the membrane. Average enrichment value ( $\bar{\beta}$ ) was used to judge the chromatographic separation efficiency, which is defined as Eq (2)

$$\bar{\beta} = \frac{\sum_{i=1}^n \beta_i}{n} \quad (2)$$

where  $\beta_i$  means the enrichment value ( $\beta_i > 1$ ) in the chromatographic effluents when the abundance of  $^{235}\text{U}$  is higher than the mean value. Firstly, we performed separation experiments using the columns under a variety of conditions. Secondly, using the front maximum enrichment value and average enrichment value enabled a good comparison of the chromatographic optimal separation conditions. Thirdly, U isotopes were subsequently separated under optimal separation conditions, the  $\beta > 1$  portion of the chromatographic effluent solution was the gold separation section. After that, the gold separation section was collected from each chromatographic effluent solution for the next stage of separation, and this operation was cycled to achieve multistage separation. Finally, based on multiple stages separation experiments, the chromatographic separation factor was calculated by using Eq (3).

$$A\alpha^n = B \quad (3)$$

where,  $A$  means the ratio of the mass of  $^{235}\text{U}$  to  $\text{U}$  in the initial solution;  $\alpha$  is the separation factor;  $n$  is the number of separation stages;  $B$  is the ratio of the mass of  $^{235}\text{U}$  to  $\text{U}$  in the separated solution[25].

### III. EXPERIMENTAL

#### 3.1 Reagents and Materials

Reagents and materials used in the experiments: Polyvinyl chloride(PVC) plastic tubes, 1 mm diameter  $\text{SiO}_2$  pellets, 1 mm diameter ABS plastic pellets,

ethanol absolute, hydrochloric acid, uranyl nitrate hexahydrate( $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ), uranyl zinc acetate ( $\text{ZnUO}_2(\text{CH}_3\text{COO})_4 \cdot 7\text{H}_2\text{O}$ ), cationic surface active agent(Hexadecyl trimethyl ammonium Bromide  $\text{C}_{19}\text{H}_{42}\text{ClN}$ ). The reagents used were all analytical pure reagents.

#### 3.2 Chromatographic column design

Two types of dynamics liquid chromatography were used in the study, which in this work were referred to as organic and inorganic columns, respectively. Their parameters are shown in supplementary file Table 1 and the column structures are shown in Fig 2.

#### 3.3 Characterization

Fourier Transform Infrared (FTIR) spectra for fillings before and after the separation experiments were obtained on Thermo Fisher Scientific Nicolet iS20 spectrophotometer (USA) in the range of  $4000\text{--}400\text{ cm}^{-1}$ . The Energy Dispersive Spectrometer (EDS) and Scanning Electron Microscope (SEM) of chromatographic fillings were carried out on Hitachi SU8100. X-ray Photoelectron Spectroscopy (XPS, Thermo Scientific K-Alpha, USA) was used to analyze the chemical composition of chromatographic fillings before and after the experiments.

#### 3.4 Design of automatic separation device

In order to enable the chromatography to realize automatic control of injection, diversion and collection, we designed a complete automatic separation device, as shown in Fig 3(a). There are four components of this automatic device: Adjustable flow systems, Switching pulse injection systems, Chromatographic separation systems (chromatography column), Time-controlled automatic shunt. Adjustable flow system equipped with SC-2556 peristaltic pump is the driving force of the entire device, which mainly used to transport the sample liquid and control the flow rate of the sample liquid. Switching pulse injection systems equipped with a three-way valve to control the gas/liquid switching feed. The injection time of liquid and gas were determined according to the experimental results. Chromatographic separation system was the central to realize separation of uranium isotopes. Time-controlled automatic shunt at the end of chromatography columns could be operated by timing and timing shunt through the fluid sensor to realize time-advancing shunt[26].

The switching pulse injection system has two internal pa-



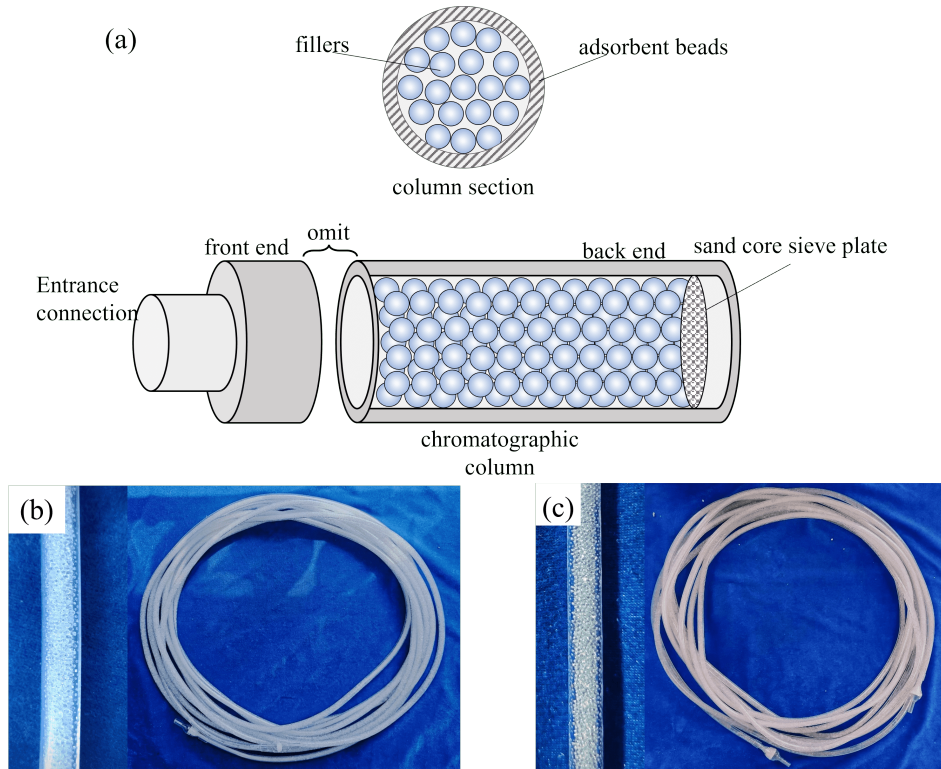


Fig. 2. (a) Schematic diagram of the structure of the column; (b) Physical diagram of the organic column; (c) Physical diagram of the inorganic column

rameters,  $T_1$  and  $T_2$ .  $T_1$  means the time of fluid injection and  $T_2$  means the time of air injection. By using the switching pulse injection system, the pre-treated sample will be fed into the column in an alternating air/liquid mode. According to the assumption in 2.3,  $^{235}\text{U}$  gradually separates from  $^{238}\text{U}$  as it moves within the column and then first flows out of the column end. At this point, the time-controlled automatic shunt automatically diverts a section of aqueous solution with a higher abundance of  $^{235}\text{U}$ , based on the  $T_3$  and  $T_4$  values obtained from previous conditional experiments. As shown in Fig 3(b), time-controlled automatic shunt has two parameters:  $T_3$  and  $T_4$ , which both have initial values. When the air section ends and solution flows out from the end of the column,  $T_3$  begins to count down, and the solution below the average abundance of  $^{235}\text{U}$  flows out of the  $T_3$  outlet. After the  $T_3$  countdown is over, the three-way valve is adjusted to the  $T_4$  position, and the  $^{235}\text{U}$  solution with higher abundance flows out from the  $T_4$  outlet, and the  $T_4$  countdown begins. Until the  $T_4$  countdown ends, the three-way valve is reset to the  $T_3$  position, and the remaining solution continues to flow out of the  $T_3$  outlet until the air section of the next pulse. In short, the separated solution collected by outlet  $T_4$  was the enrichment solution and was collected into the enrichment solution cells.

However, a single stage of separation could not achieve the  $^{235}\text{U}$  abundance for nuclear fuel fabrication, therefore, it is necessary to install a reflux device outside the chromatographic separation system to achieve multistage separation.

Generally, in the  $n^{\text{th}}$  stage of separation, the adjustable flow system makes the depleted stream flow back to the  $(n-1)^{\text{th}}$  stage sample cell, and the enrichment flows into the cell to be separated, waiting for the  $(n+1)^{\text{th}}$  stage of separation, and so on[27], as shown in Fig 3(c).

## IV. RESULTS AND DISCUSSION

### 4.1 Organic chromatographic column for U isotope separation

ABS plastic is a kind of ternary copolymer composed of any content of acrylonitrile (A), butadiene (B), styrene ethenylbenzene (S), which has the advantages of strong corrosion resistance, high toughness, and easy-to-obtain raw materials, etc. This material has a wide range of applications in the manufacturing industry and chemical industry, including mechanical, electrical, 3D printing and other manufacturing industries, as well as in the chemical industry[28–30]. In order to investigate the effect of organic functional groups on isotope separation, avoid other chemical reactions between uranyl nitrate and fillings, and enable the fillings to be reused for a long period of time, the organic columns were packed with ABS plastic spheres with a diameter of 1.0 mm.

In the previous study of this research group[26, 31], researchers have conducted a series of studies on temperature-enabling kinetic liquid chromatography, since both silica and ABS fillings are not adsorbent to uranyl ions, so many of



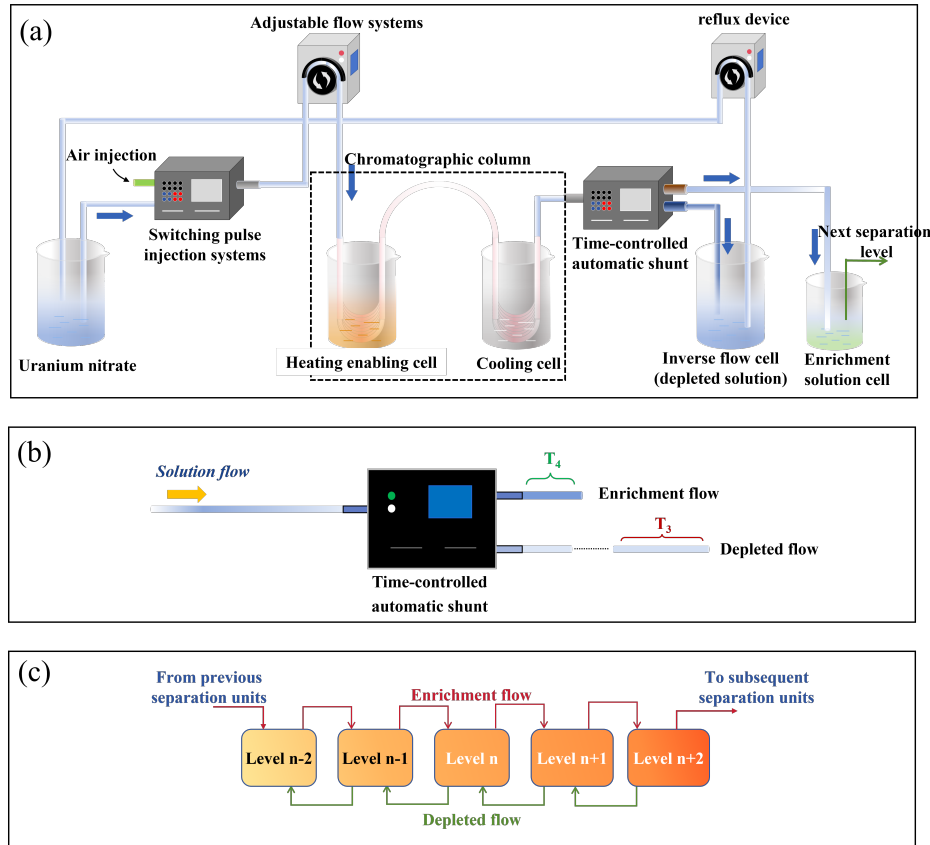


Fig. 3. (a) Schematic diagram of the automatic separation device; (b) separation principle of the time-controlled automatic shunt; (c) Flow chart of chromatographic device multi-stage separates U isotopes

working conditions can be followed in this paper. In those work, the optimal flow rate of the sample inside the 10m-type column was 5.698 mL/min, but it is obviously not suitable for organic column with larger internal diameters. The linear velocity of the sample in the column can be calculated by Eq 4 and the sample flow rate suitable for organic columns can be deduced inversely.

$$l = \frac{QH}{V_{column} - V_{fillings}} \quad (4)$$

Where,  $l$  (cm/min) is the linear velocity of the solution inside the column;  $Q$  (mL/min) is the flow rate of the solution;  $H$  is the length of the column;  $V_{column}$  is the volume of the column; and  $V_{fillings}$  is the total volume of the fillings. The previous column was calculated that sample flow rate was 15 mL/min. In order to make the flow rate of the mobile phase of fillings in organic columns same, the flow rate of mobile phase for the organic column in this paper was also 15 mL/min. The work built on prior experiments, establishing the injecting mode was set at 20mL (injection) for 80s, and then switched to gas (air); when the solution flowed out in strands at the outlet end of the column (gas injection for about 100s), the inlet end of the column was switched to liquid injection, and this was repeated. These time data were set

in the switching injection system (Fig 3(a)) to realize the purpose of gas/liquid switching injection.

#### 4.1.1 Characterization of ABS fillings

Characterization was carried out on the type chromatographic column fillings before and after separation experiments. SEM-EDS characterization showed that ABS plastic pellets were in the shape of a sphere with a little layer structure on the surface, and the surface morphology of the filling before and after the experiment was almost unchanged, and the adsorption of elemental U was not observed (at pH=2). Although the adsorption of U was not detected in the EDS characterization, XPS results showed that there was still a trace amount of U(VI) remaining in ABS plastic after the experiment.

The description of ABS fillings' characterization is shown in supplementary file.

#### 4.1.2 Effect of pH on separation

Comprehensive previous experiences, the pH value of the solution has a great influence on the separation, ABS plastic pellets for the first time as a chromatographic filling, to determine the optimal conditions for its use is crucial. When the solution pH value is 2.5, the main of uranium in the solution is uranyl ion ( $UO_2^{2+}$ ). When pH>2.5, with the increase of pH value, the uranyl ion ( $UO_2^{2+}$ ) in the solution begins to hydrolyze, forming a multinuclear or even cage structure, and finally generating the hydroxide precipitation[32]. In order to



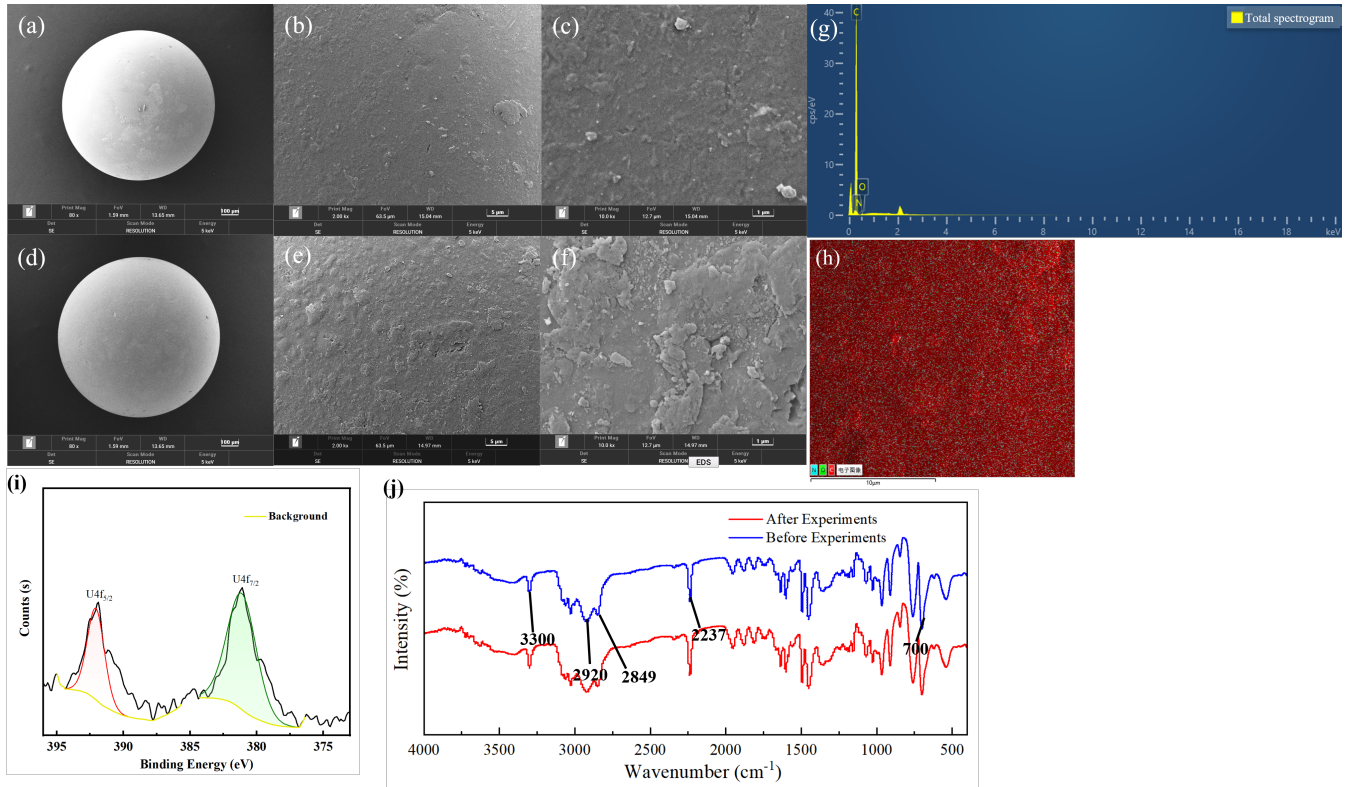


Fig. 4. SEM-EDS characterization of ABS fillings before and after experiments (a) 100 $\mu\text{m}$  before experiments; (b) 5 $\mu\text{m}$  before experiments; (c) 1 $\mu\text{m}$  before experiments; (d) 100 $\mu\text{m}$  after experiments; (e) 5 $\mu\text{m}$  after experiments; (f) 1 $\mu\text{m}$  after experiments; (g) EDS total spectrum after experiments; (h) EDS electronic spectrum after experiments; (i) XPS characterization; (j) FTIR characterization

determine the more suitable acidity for organic type columns, the experiment used uranyl nitrate solution of 15-200ppb and divided it into three groups with pH values set at 2, 4 and 7, respectively. Meanwhile, in order to exclude other interferences, the columns were not temperature-enabled in this experiment, and the results obtained are shown in Fig 5.

Measurements of U isotope concentrations using ICP-MS are subject to some uncertainty. In Fig.9, the light-colored area indicates the fluctuation ranges of isotope concentration. Moreover, the quality and dispersion of  $\beta_{\text{max}}$  was analyzed by type-A uncertainty, which is defined as Eq 5.

$$uA = \sqrt{\frac{\sum_{i=1}^n (s_i - \bar{s})^2}{n(n-1)}} \quad (5)$$

where,  $uA$  stands type-A uncertainty;  $s_i$  denotes the  $i^{\text{th}}$  test result of a sample;  $\bar{s}$  means average value of a sample test;  $n$  is the number of tests for a sample.

The results showed that at pH = 2, uranyl ions were mainly concentrated in the front and back end of the column effluent, and the best separation section was at the 6 ~ 8 mL and 10 ~ 14 mL,  $\beta_{\text{max}} = 1.0243$ ,  $uA = 5.4419 \times 10^{-2}$ ,  $\bar{\beta} = 1.0150$ . At pH=4, the concentration of uranyl ions fluctuated continuously with the effluent volume, and the best separation section was at the 2 ~ 6 mL and 8 ~ 10 mL,  $\beta_{\text{max}} = 1.0175$ ,  $uA = 1.7082 \times 10^{-2}$ ,  $\bar{\beta} = 1.0093$ , and its separation effect

was weaker than that of the other two groups of experiments; At pH=7, uranyl ions were also mainly concentrated in the first and last of the effluent, and the optimal separation section was in the 8 ~ 16 mL,  $\beta_{\text{max}} = 1.0242$ ,  $uA = 1.2595 \times 10^{-2}$ ,  $\bar{\beta} = 1.0148$ . The comprehensive results showed that pH = 2 was the most suitable acidity for the organic type column.

At pH=4, the species of uranium in solution are  $\text{UO}_2^{2+}$  and  $\text{UO}_2(\text{OH})^+$ , the internal environment of the chromatographic column was complicated, resulting in irregular change trend of U isotope concentration, as shown in Fig 5(b), and the degree of enrichment is lower than the other two groups, pH=2 and pH=7. Because of the existence of liquid membrane and the adsorption of uranium by ABS fillings, the uranium in the solution remained in the residual liquid membrane on the surface of the fillings every time the solution flows through the chromatographic column. At the same time, the chromatographic injection method used in this paper is gas/liquid switching injection (1.2), which makes the next solution pulse through the column will carry the residue of the previous solution pulse. At pH=7, the main species of U were  $\text{UO}_2(\text{OH})_2$ , therefore, compared with pH=4, the concentration of U changes more regularly. From Fig 5(a) (c), it can be clearly observed that the concentration of U with the change of effluent volume showed a trend of decreasing and then increasing, the concentration of the first section of the chromatographic effluent volume is generally higher, indicating that there will be a residue in the solution flow through the column, and af-



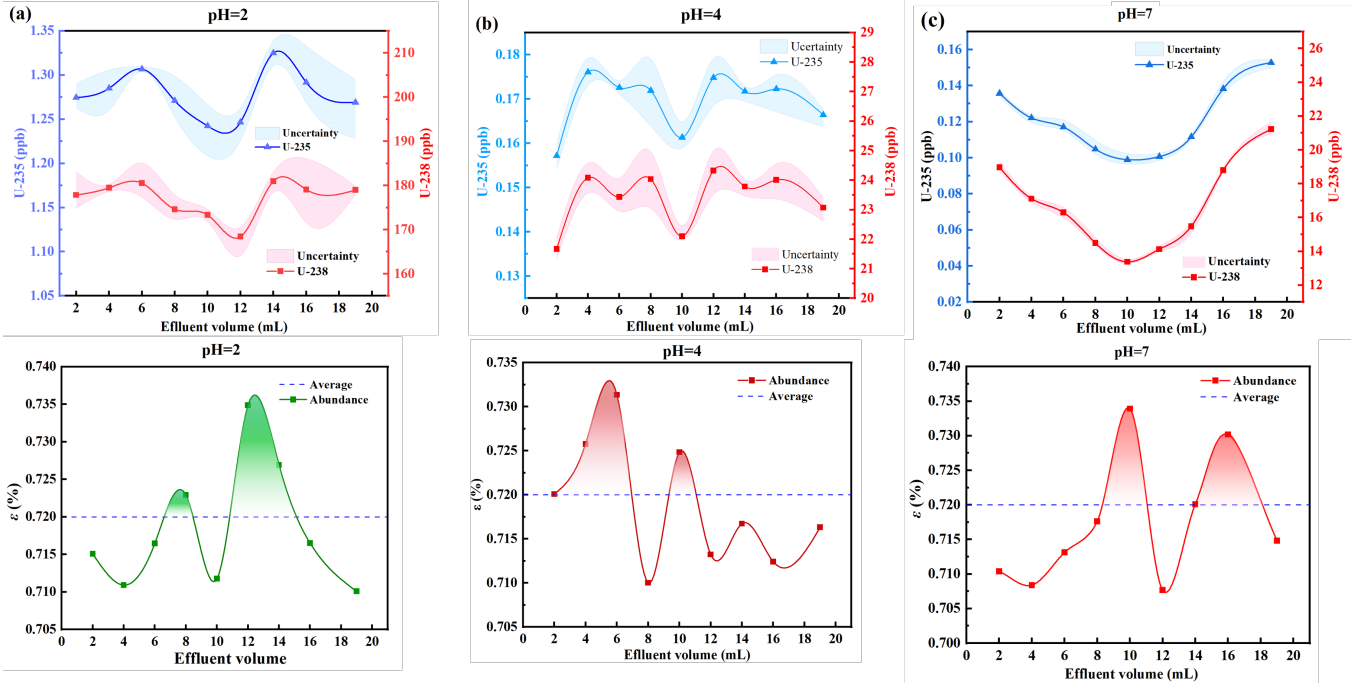


Fig. 5. Effect of pH on the concentration of U isotopes and abundance of  $^{235}\text{U}$  in chromatographic column. (a) pH=2; (b) pH=4; (c) pH=7

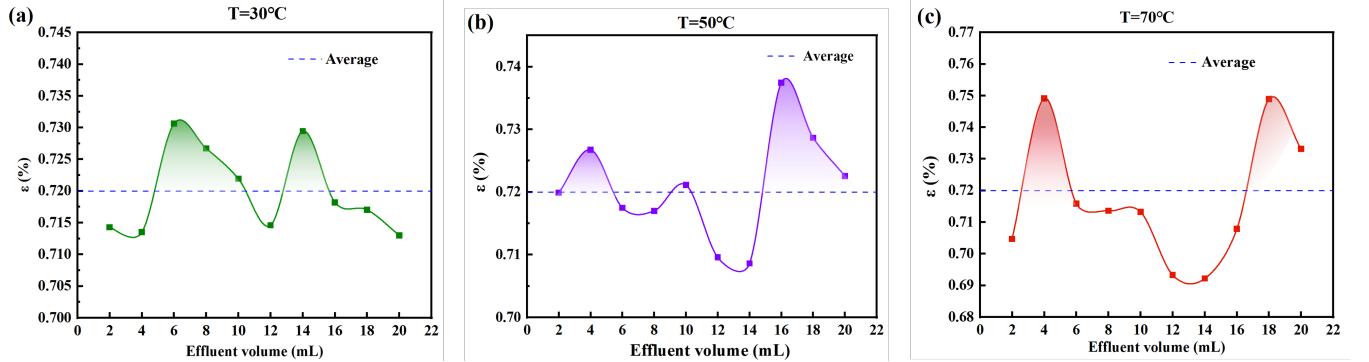


Fig. 6. Effect of temperature on the separation of uranium isotopes (a)  $T=30^\circ\text{C}$ ; (b)  $T=50^\circ\text{C}$ ; (c)  $T=70^\circ\text{C}$

ter chromatographic separation, the concentration of U will be concentrated in the second half.

#### 4.1.3 Effect of enabling temperature on separation

In this paper, the pipe used for preparing the chromatographic column is made of PVC material, which has high toughness, transparency and corrosion resistance, and the pipe wall thickness is only 2 mm, so the column can be temperature-enabled well. In the experiment, the solution temperature has a great influence on the functional groups on the fillings surface and the formation of the liquid membrane. By heating and cooling organic-type column using the temperature-enabling cell in Fig 3(a), the flow of uranyl ions blocked by column fillings will change periodically, which will facilitate the separation of U isotopes. Theoretically, the larger the temperature difference between the enabling and cooling cell, the more significant the gain in U isotope separation, but when the temperature reaches  $75^\circ\text{C}$  or more ABS

plastic will deform[33, 34]. Therefore, in this paper,  $30^\circ\text{C}$ ,  $50^\circ\text{C}$ , and  $70^\circ\text{C}$  were used to be the enabling temperature of the chromatography. In the experiment, uranyl nitrate solution of 50 ppb and pH=2 was used as the sample to be separated, and the separation results were shown in Fig 6.

The results showed that the best separation sections of U isotopes on the organic column after temperature enabling were concentrated at the front and rear ends of the effluent volume, which were calculated as follows:  $\beta_{\max} = 1.0150$  and  $\bar{\beta} = 1.0101$  at  $T = 30^\circ\text{C}$ ;  $\beta_{\max} = 1.0231$  and  $\bar{\beta} = 1.0117$  at  $T = 50^\circ\text{C}$ ; and  $\beta_{\max} = 1.0449$  and  $\bar{\beta} = 1.0373$  at  $T = 70^\circ\text{C}$ . With the increase of assignment temperature, the separation efficiency of organic column for U isotopes was also increased. The maximum enrichment and average enrichment were much larger than those of other groups when the enabling temperature was  $70^\circ\text{C}$ . Therefore,  $70^\circ\text{C}$  was selected as the best separation enabling temperature, and  $2 \sim 4$



Table 1. Experimental data and results of the organic chromatographic column

test	Solution flow rate	Solutions and pH	Enabling temperature	Maximum front enrichment value /separation factor	Type-A uncertainty	Average enrichment
Enabling Temperature Conditions Experiment	15mL/min	Uranyl nitrate solution pH=2 pH=4 pH=7	without temperature-enabling	$\beta_{max} = 1.0250$	$5.4419 \times 10^{-2}$	$\bar{\beta} = 1.0156$
				$\beta_{max} = 1.0180$	$1.7082 \times 10^{-2}$	$\bar{\beta} = 1.0126$
				$\beta_{max} = 1.0242$	$1.2595 \times 10^{-2}$	$\bar{\beta} = 1.0148$
pH value conditioned experiment	15mL/min	Uranyl nitrate solution pH=2	30°C	$\beta_{max} = 1.0150$	-	$\bar{\beta} = 1.0101$
			50°C	$\beta_{max} = 1.0236$	-	$\bar{\beta} = 1.0116$
			70°C	$\beta_{max} = 1.0445$	-	$\bar{\beta} = 1.0373$
multistage separation test		Uranyl nitrate solution pH=2	70°C	$\bar{\alpha} = 1.0184$	$5.4816 \times 10^{-5}$	-

mL and 16 ~ 20 mL were the best separation sections for the chromatographic effluents.

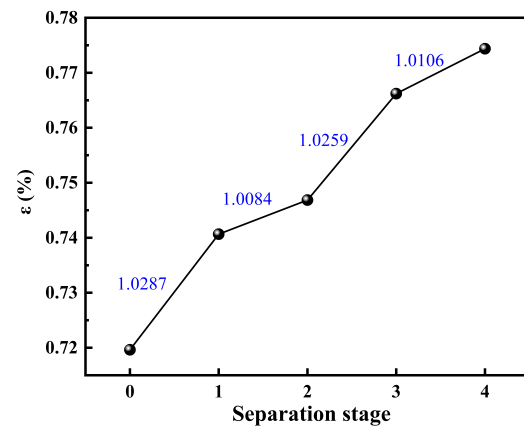
In section 2.1, the theory indicated that  $^{235}\text{UO}_2^{2+}$  is lighter than  $^{238}\text{UO}_2^{2+}$ , which cause  $^{235}\text{UO}_2^{2+}$  in the liquid membrane would more easily be moved into mobile phase and the  $^{235}\text{U}$  abundance in first few chromatography effluent should be higher. However, in the first few chromatography effluents (Fig. 5, 6) were lower than 0.72%. Actually, this phenomenon is correct. Since the sample was pulsed in the experiment, the previous pulse will remain on the column filling surface, and the residual solution will have a lower abundance of  $^{235}\text{U}$  and a higher abundance of  $^{238}\text{U}$ . This was reflected in the abundance of  $^{235}\text{U}$  below 0.72% in the first few experimental data points.

#### 4.1.4 Multi-stages separation experiments

Through the above condition experiments, this paper finally determined the optimal working conditions of the organic column as: solution flow rate of 15 mL/min, pH = 2, enabling temperature of 70°C, and the optimal separation segments in the chromatographic effluent volume of 2 ~ 4 mL and 16 ~ 20 mL. The effluent can be accurately collected using the time-controlled automatic shunt system in Fig 3(a). The original sample was uranyl nitrate solution with a natural abundance of 50 ppb, and the experimental results are shown in Fig 7,  $\alpha_1 = 1.0287$ ,  $\alpha_2 = 1.0084$ ,  $\alpha_3 = 1.0259$ ,  $\alpha_4 = 1.0106$ ,  $\bar{\alpha} = 1.0184$ , and type-A uncertainty was  $5.4816 \times 10^{-5}$ . In this way, the abundance of  $^{235}\text{U}$  could reach 3% through 79 stages separation. The results showed that the abundance of  $^{235}\text{U}$  continued to increase during the step-by-step separation, but the separation factors of stage 2 and stage 4 are relatively small. Moreover, compared with that in 3.1.3, the separation factors were inferior to that in one stage separation. The reason for this phenomenon may be due to the presence of a three-way valve in the time-controlled shunt system at the outlet end of the column, in which the outflow solution produces a Bernoulli phenomenon, which leads to a reduction in the flow rate of the solution, stagnation, and mixing of the front and back solutions, which results in a decrease in the abundance. Table 1 shows all the experiments done with the organic column. And type-A uncertainty is also displayed in it.

## 4.2 Inorganic chromatographic column for U isotope separation

In the previous work of researchers[26, 31], the column was filled with  $\text{SiO}_2$  pellets. Therefore, some experimental

Fig. 7.  $^{235}\text{U}$  abundance under multi-stages separation

conditions were followed in this paper for the study of inorganic chromatographic columns, and the working conditions were set as follows: solution flow rate of 15 mL/min, pH=2, and temperature of the enabling cell at 50°C.

### 4.2.1 Characterization of $\text{SiO}_2$ before and after experiments

SEM-EDS characterization showed that the inorganic fillings( $\text{SiO}_2$ ) were smooth spheres, the surface of the fillings was still smooth after separation experiments, and no U adsorption was observed. The FTIR results indicated that hydroxyl groups were produced on the surface of the  $\text{SiO}_2$  filling after the experiment. And XPS determination showed the filling has a trace adsorption of uranium after experiments.

The characterization results of  $\text{SiO}_2$  fillings were shown in supplementary figure 2.

### 4.2.2 Single separation of uranium isotopes

Uranyl nitrate solution of 50ppb and pH=2 was used as the separation sample solution. The column enabling temperature was 50°C and the injection rate was 15 mL/min. The effluent was collected at the exit of the chromatographic column every 2 mL, and a total of 11 samples (including the original solution) were detected by an inductively coupled plasma mass spectrometer (model: ICAPRQ02625), and the results were shown in Fig 8. It can be seen from the results that the



separation effect of  $^{235}\text{U}$  and  $^{238}\text{U}$  is significant in the 5 ~ 11 mL of the chromatographic effluent, so the optimal separation of U isotopes in the inorganic column is the 5 ~ 11 mL. In Fig 8(b), The enrichment reached the maximum at the effluent of 10 mL, i.e.,  $\beta_{\max} = 1.0171$ . While in the optimal separation section,  $\bar{\beta} = 1.0142$ .

In addition, regarding Fig 8(b), adsorption of uranyl ions by silanol groups on the surface of  $\text{SiO}_2$  filling causes  $^{235}\text{U}$  to have a longer retention time in the column. As a result, uranium abundance appeared in the middle-to-late section of the chromatographic effluent volume, and the double-peaks overlap.

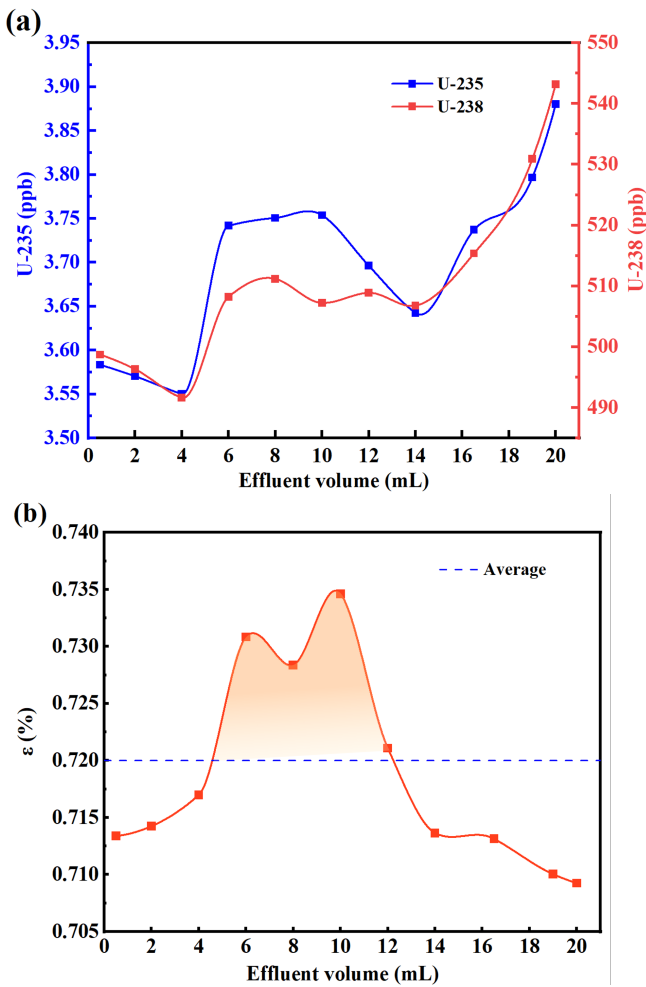


Fig. 8. (a) Concentration of  $^{235}\text{U}$  and  $^{238}\text{U}$  in effluent solution with effluent volume; (b) Abundance of  $^{235}\text{U}$  in effluent solution with effluent volume

#### 4.2.3 Multi-stages separation experiments

According to the work in section 4.2.2, the best separation section for U isotopes is in the 5 ~ 11 mL of the chromatographic effluent, which means that after each stage of separation, the middle 3/10 of the solution can be collected as the enrichment solution. The self-constructed automatic control shunt system could well realize the automatic separation of each section of the effluent, and realize automated and con-

tinuous work, and no manual duty required.

After four stages of separation, the results were shown in Fig 9. Calculating the separation factors for each stage by Eq 3, it had been obtained that  $\alpha_1 = 1.007$ ,  $\alpha_2 = 1.004$ ,  $\alpha_3 = 1.02$ ,  $\alpha_4 = 1.009$ , and  $\bar{\alpha} = 1.011$ , which was not as good as the organic column, but comparable to the gas diffusion method. To achieve  $^{235}\text{U}$  abundance of 3%, a 112-stage separation should be required. The results showed that the abundance of  $^{235}\text{U}$  continued to increase during the stepwise separation. Similar to the organic columns, the second stage of separation remained the least effective.

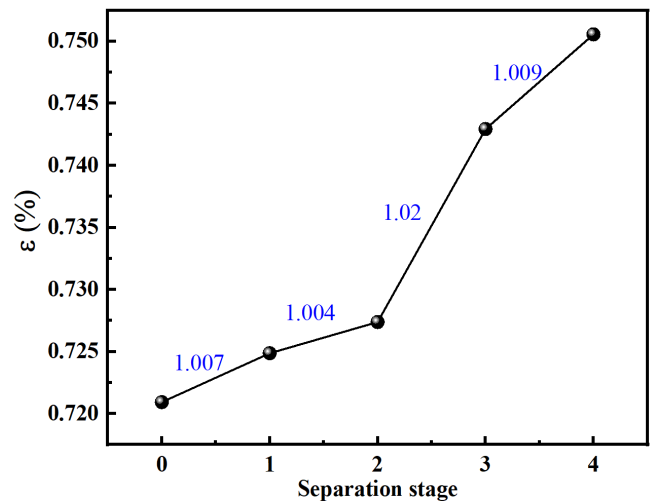


Fig. 9. Multi-stage separation of uranium isotopes by inorganic column

#### 4.2.4 Experiments in strong acid environments

According to the characterization in 3.2.1, a small amount of silica hydroxyl groups generated on the surface of  $\text{SiO}_2$  filling during the separation process (Fig 8). In order to verify the importance of silica hydroxyl groups in the separation process, in this paper, the pH value of the solution to be separated was adjusted to 0.1, in which case the silica hydroxyl groups on the surface of  $\text{SiO}_2$  were suppressed to a great extent[35], which was used to determine the effect of silica hydroxyl groups on the separation (Fig 10). Experimentally, 15ppb, pH=0.1 uranyl nitrate solution was used as the separation sample solution, and other working conditions were consistent with 3.2.2, and the experimental results are shown in Fig 11.

As can be seen in Fig 11(a), the concentration trends of  $^{235}\text{U}$  and  $^{238}\text{U}$  were nearly the same,  $\beta_{\max} = 1.0122$  and  $\bar{\beta} = 1.0056$ . The difference from that in Experiment 3.1 was very large, the separation efficiency was poor, and the abundance change curves (Fig 11(b)) did not form a regular peak. Therefore, when the silica hydroxyl group was inhibited during the separation process, the separation effect was insignificant, which successfully proved that the presence of silica hydroxyl group had a positive benefit on the separation effect. In other words, moderate acidity (pH=2 or so) is favorable for the separation of U isotopes; too high acidity (pH<0.1) is unfavorable for the separation of isotopes.



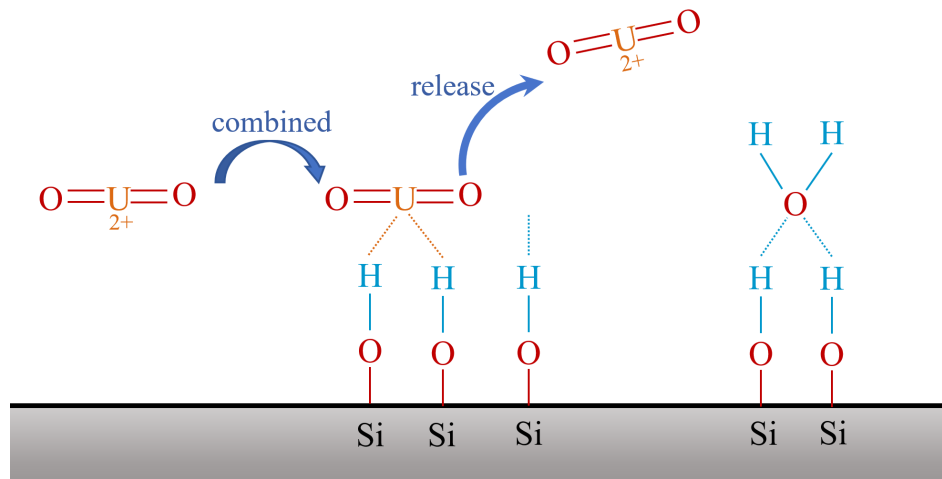


Fig. 10. Behavior of uranyl ions passing through silicon hydroxyl

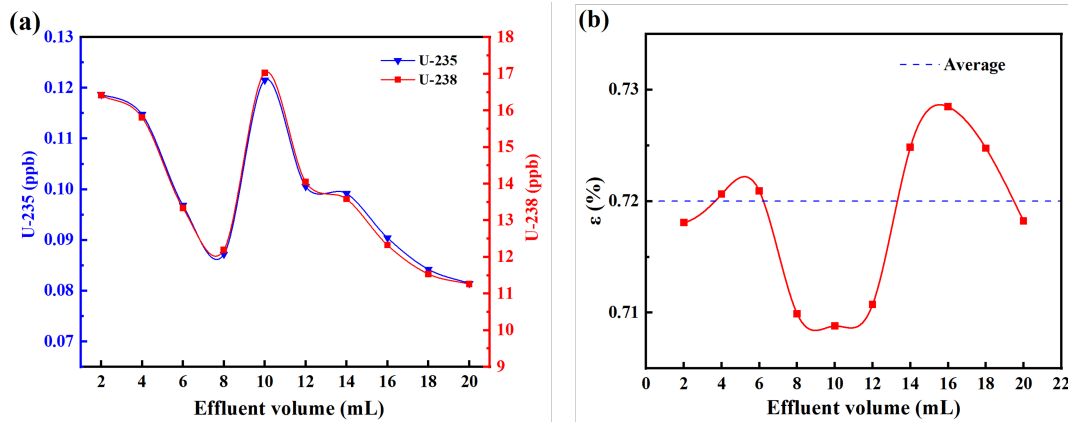


Fig. 11. Effect of silicon hydroxyl group on separation at pH 0.1. (a) Variation of uranium isotopes at the effluent end of the chromatographic column; (b) Distribution of  $^{235}\text{U}$  in the chromatographic column

### 4.3 Separation mechanisms

The experiments in 3.1 and 3.2 had demonstrated that organic and inorganic chromatographic column were able to separate U isotopes efficiently, but the separation mechanisms still need to be explored. In the following, a series of experiments are designed to verify the hypotheses made in the previous section: 1. A liquid membrane will be generated between the fillings and the mobile phase within the chromatography, which will have different blocking effects on particles with different masses; 2. There is a process of trapping and releasing of flow-through particles by the functional groups generated on the surface of the fillings.

In order to verify that the column can separate other particles with different mass, the U-Zn separation experiment was designed in this work. A 50ppb solution of zinc uranyl acetate, pH=2, was used as the sample to be separated, and the experimental conditions were the same as those in 3.1. Because the relative atomic mass of  $\text{UO}_2^{2+}$  in the solution is 270 and that of  $\text{Zn}^{2+}$  is 65.38, both of them have the same valence, neither of them reacts chemically with other substances

within the chromatogram, and the difference in mass is obvious, which is well in line with the requirements of the validation experiment. The distribution of Zn and U in the effluent was shown in Fig 12(a)(b).

Eq 1 was modified to the following form for use in describing the capacity of chromatography on the separation of U and Zn:

$$\beta = \frac{{}_s\text{Zn}/{}_s\text{U}}{{}_o\text{Zn}/{}_o\text{U}} \quad (6)$$

In Eq 6,  ${}_s\text{Zn}/{}_s\text{U}$  is the mass concentration ratio of Zn-U in the chromatographic effluent.  ${}_o\text{Zn}/{}_o\text{U}$  is the mass concentration ratio of Zn-U in the original sample. It was calculated that  $\beta_{\max} = 1.3253$ . Compared with the U isotopes, the mass difference between  $\text{UO}_2^{2+}$  and  $\text{Zn}^{2+}$  is much larger and the separation effect is more obvious. It was also proved that the liquid membrane can effectively separate ions of different masses.

Otherwise, to verify the role of the liquid membrane in sep-



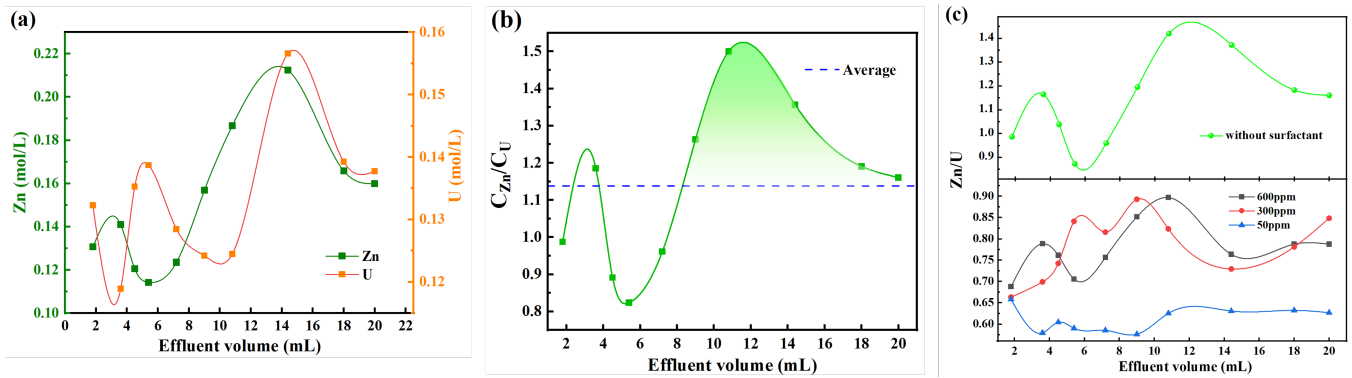


Fig. 12. (a) Concentration changes of U and Zn in column effluent; (b) Distribution of Zn-U in chromatographic column

Table 2. Data and parameters of inorganic chromatographic column separation experiments

test	flow rates	Solutions and pH	enabling temperature	Maximum front enrichment value /Separation factor	Average enrichment
U isotopes primary separation	15mL/min	Uranyl nitrate solution pH=2	50°C	$\beta_{max} = 1.0224$	$\bar{\beta}= 1.0162$
U isotopes multistage separation		Uranyl nitrate solution pH=2		$\bar{\alpha} = 1.011$	-
Strong acid environment		Uranyl nitrate solution pH=0.1		$\beta_{max} = 1.0122$	$\bar{\beta} = 1.0068$
Zn-U separation		Zinc uranyl acetate solution pH=2		$\beta_{max} = 1.3253$	-
surfactant		Zinc uranyl acetate solution 50ppm (add surfactant) 300ppm pH=2 600ppm		$\beta_{max} = 1.0773$ $\beta_{max} = 1.1394$ $\beta_{max} = 1.1519$	- - -

aration process, the experiment used 50ppb, pH=2 solution of zinc uranyl acetate as the sample, adding different concentrations of cationic surfactant (cetyltrimethylammonium chloride:  $C_{19}H_{42}ClN$ ) in the sample, to observe the influence of the change of the liquid membrane on the separation effect, and the results of the experiments were shown in Fig 12(c).

The structure of surfactants can be viewed as a match-like configuration, shown in supplementary file Fig. 3(a). The "matchstick" as a hydrophobic group repels water molecules, such as R-(alkyl), while the hydrophilic group is the "match-head" which attracts water molecules, such as -OH, -NH<sub>2</sub>. This special structure makes the surfactant molecule soluble in water at one end and tends to escape from water at the other end, so as to reduce the tension between water molecules. When used in the mobile phase of a chromatographic column, the liquid membrane formed on the fillings surface is affected[36], as shown in supplementary file Fig. 3(b).

The experimental results showed that the separation effect of chromatography was very poor when the concentration was 50 ppm, and  $\beta_{max}$  was only 1.0773; when the concentration was 300 ppm, the separation effect of chromatography was better, and  $\beta_{max}$  could reach 1.1394; when the concentration was 600 ppm, the separation effect was decreased  $\beta_{max} = 1.1519$ . At the same time, with the increase of the concentration of the surfactant, the formation of micelles within the mobile phase, which substantially increased the flow impedance, and Zn was significantly more affected than  $UO^{2+}$ , and the position of the chromatographic peak was shifted backwards. The reason was as followed: When

the concentration of surfactant was 50ppm, the water tension was unevenly weakened, the liquid film became irregular and thin, the separation effect was greatly reduced, so there was no obvious chromatographic peak in the effluent curve. At 300ppm, the surfactant groups were all over the surface of the packing material, and the ions in the mobile phase were subjected to increased resistance. Although there was a separation effect, the outflow curve of the experimental results could not form regular chromatographic peaks. When the concentration of surfactant was 600ppm, the surfactant in the solution would exist in the form of micelles, and the resistance to flow would further increase, and there would be obvious double chromatographic peaks. Finally, the experiment was successful to prove the participation of liquid membrane in the separation process. It was experimentally verified that the inorganic column was effective for the separation of U isotopes, and the abundance of U isotopes showed an increasing trend in the multi-stage separation experiments, which is expected to realize the industrialized production. The hypothesis of the liquid membrane model proposed in the previous paper was also verified, and the chromatographic separation mechanism was explored. Table 2 shows the relevant experimental parameters of this paper using inorganic column.



## V. CONCLUSION

In this paper, chromatographic columns with two types of organic and inorganic fillings were prepared and applied to the U isotopes separation work to obtain the separation efficiency and the separation mechanism was discussed. ABS plastic as fillings for organic column are cost-effective and flexible, ideal for prolonged use, which could reach a separation factor greater than inorganic column. However, it has exhibit lower mechanical strength, and limited surface modification options. SiO<sub>2</sub> pellets as fillings for inorganic column offer high mechanical strength, excellent chemical stability, and large surface area. Nevertheless, they are potentially brittle and the inorganic column's separation efficiency was not as good as the organic column.

In organic column experiments, the chromatography optimal working condition were as follow: injection flow rate=15 mL/min, pH=2, enabling temperature=70°C and the golden separation segments were 35 mL and 1720 mL from the chromatographic effluent. Multi-stage separation experiments showed U isotopes separation factor was 1.0184, and 79 separation stages were needed for <sup>235</sup>U abundance reach to 3%.

According to inorganic column experiments, the chromatography optimal working conditions were firstly deter-

mined by previous studies, which were as follow: injection flow rate=15 mL/min, pH=2, enabling temperature=70°C and the golden separation segments were 511mL from the chromatographic effluent. Multi-stage separation experiments indicated that U isotopes separation factor was 1.011, and 113 separation stages were required for enriching <sup>235</sup>U abundance to 3%.

Based on characterization results and separation mechanism experiments, liquid membranes and surface functional groups on fillings did participate in separation processes. For industrial production, uranyl nitrate feedstock could be applied directly, potentially skipping UF<sub>6</sub> preparation in gas centrifugation. SEM-EDS, XPS, and FTIR analyses showed SiO<sub>2</sub> and ABS adsorb slight amounts of uranium without affecting fillings properties, allowing long-term column reuse. Therefore, combining organic and inorganic dynamic liquid chromatography provides a cost-effective, eco-friendly, and efficient method for U isotope separation. The researches also provided new ideas for the chromatography and isotope separation field.

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